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THE EFFECT OF CHROMIUM (Cr) ALLOYING ADDITION ON THE MICROSTRUCTURE OF TITANIUM ALUMINIDES ALLOYS RELATED TO ITS OXIDATION BEHAVIOUR

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ABSTRACT
A number of selected compositional variations of titanium aluminides alloys have been produced by arc-melting process in a specially-designed and locally-made furnace. The alloy samples were then oxidized in air at 900°C for 50 hours inside a muffle furnace. Unlike earlier investigations, in this study the microstructures of the alloys have been characterized using SEM/EDS to link the effect of microstructures on the oxidation behavior. The oxidation kinetics was also studied by determining the weight gain of the alloy samples during the oxidation process. Ti-42Al-27Cr alloy (in at.%) with its protective Al_2O_3 scale due to its Laves phase has been observed to have the lowest oxidation rate. On the contrary, the existence of the β phase in the Ti-45Al-10Cr resulted in a higher oxidation rate. Reinforcing the earlier claim that the transition for TiO stability to alumina stability occurs at approximately 50 at.% Al, this study also found that the protective alumina scale was evident on the surface of its Ti-50Al alloy.

Keywords: titanium aluminides; arc-melting furnace; microstructures; Laves phases; oxidation resistance

INTRODUCTION
Titanium aluminides alloys have been considered as promising structural materials for high temperature applications in aerospace, automotive, chemical process and power generation industries due to their high specific properties such as high-temperature strength, good creep and fatigue resistance, low density, high stiffness, and high modulus. The potential applications include turbine blades, turbine wheels, high-pressure compressor blades, impellers, exhaust valves, turbocharger rotors and rotating parts of engine [8].

As structural materials, the alloys will have not only to stand mechanical stress but also be exposed to aggressive atmospheres/hot gases. However, excellent mechanical properties are not sufficient to ensure the success of the materials, but oxidation resistance is a key issue in high-temperature applications. In development of alloys, the oxidation resistance has been given very high consideration as it plays a fundamental role in determining lifetime of the materials [2].

To improve the oxidation resistance of the alloys, many investigations have been carried out, dealing with the alloying addition of third elements, pre-treatment at low oxygen pressures, fluidized bed treatment, Al-pack cementation, Al and Cr simultaneous pack cementation, sulfidation treatment, overlay coating, and ion implantation [11]. In this present study, an elemental alloying addition has been attempted.

Of all elements that have been added to binary Ti-Al alloys to enhance their oxidation resistance, chromium (Cr) is unique in that relatively small amounts (> 4 at. %) are sufficient to form a protective alumina scale and suppress the formation of nonprotective rutile oxide scale. It is called as 'chromium' effect. The addition of Cr to the alloys introduces a second phase, a $Ti(Cr,Al)_2$, Laves phase [4,10,12].

The properties of the alloys are strongly composition and microstructure-dependent including its oxidation resistance. The microstructures of the alloys can be divided generally into three types: fully lamellar, duplex and equiaxed gamma [9]. Since each of the microstructures type gives different oxidation resistance, the purpose of the present study is to produce and characterize microstructures on compositional variations of titanium aluminides alloys such as Ti-50Al, Ti-53Al, Ti-60Al, Ti-65Al, Ti-52Al-5Cr, Ti-45Al-10Cr, Ti-45Al-15Cr and Ti-42Al-27Cr alloys (in at.%). Secondly, the other objective of this work is to investigate the effects of chromium alloying addition on microstructures of the alloys. The third objective of this study is to systematically elucidate the oxidation process in air at 900°C for 50 hours on Ti-50Al, Ti-60Al, Ti-52Al-5Cr, Ti-45Al-10Cr and Ti-42Al-27Cr alloys as representatives of their groups.

OXIDATION PROCESS
Oxidation can lead to a loss of load-bearing capacity in a component by the reduction of metallic cross section and, for many high-temperature applications, is the primary factor limiting service life [7]. Fig.3 shows schematically the mechanism of oxidation on binary titanium aluminides alloy. The scale forming alloying elements (Ti and Al) diffuse to the interface of environment and alloy. The oxygen gases of

environment diffuse in the reverse direction. The oxygen gases combines with alloying elements to form precipitated oxide particles [1]:

$$aM + 1/2bO_2 \rightarrow M_aO_b \quad (1)$$

The process has been known as internal oxidation schematically shown as step c in Fig.2. The necessary condition for the occurrence of internal oxidation phenomenon is the free energy (ΔG^{θ}) of formation (per mole O_2) for the solute metal oxide, M_aO_b, must be more negative than the free energy (ΔG^{θ}) of formation (per mole O_2) for the base metal oxide [1].

The critical solubility product of M_aO_b, for the nucleation of precipitates has been established at a reaction front (parallel to the specimen surface) by the inward diffusing oxygen and the outward diffusion of solute. Nucleation of the oxide precipitate occurs and a given precipitate grows until the reaction front moves forward and depletes the supply of solute M arriving at the precipitate. In titanium aluminides alloy, M can refer to Ti or Al, so that the oxide-precipitates formed can be either TiO_2 (TiO) or Al_2O_3 as shown in Fig.3. It has been expected that the oxide scale was Al_2O_3 due to its thermodynamic stability and protective oxide continuity [1].

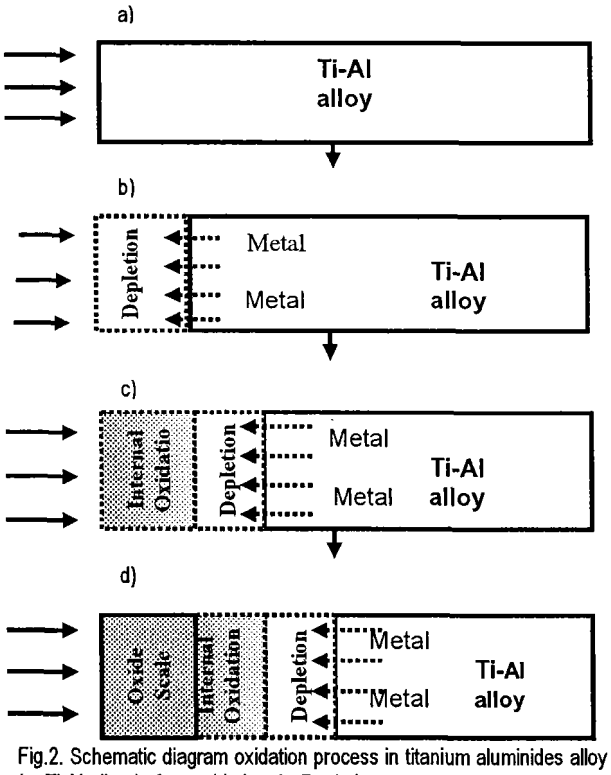

Fig.2. Schematic diagram oxidation process in titanium aluminides alloy (a. Ti-Al alloy before oxidation; b. Depletion process occurs; c. Internal oxidation occurs; d. Oxide scale formation).

During the oxidation of ternary titanium aluminides alloys, Al is depleted and Cr is enriched at the alloy/scale interface (Ti maybe depleted or enriched). The depletion of Al results from the consumption of Al to form protective alumina scale. The enrichment of Cr occurs because Cr is much noble in oxygen than Ti or Al, and is not extensively consumed to form oxide scale [4,5]. A protective oxide scale is produced if it consists of a uniform and thermodynamically stable Al_2O_3 oxide scale (Fig.3b).

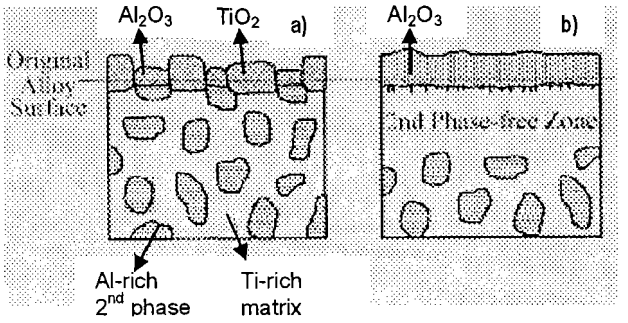

Fig.3. A schematic shows a) formation a non-uniform, non-protective TiO_2 and AL_2O_3 scale; b) Al-rich second phase in support of protective Al_2O_3 oxide scale formation [7].

EXPERIMENTAL

Titanium aluminides alloys used in the present study have been prepared at the School of Materials and Mineral Resources Engineering, USM, Penang, Malaysia. Several necessary steps were taken to produce the alloys. Powders of the required metals were first weighted according to the intended compositional variations (Table 1). The powders were then mixed under inert atmosphere for 5 – 6 hours to obtain a uniform mixture. A Carver compaction equipment was used to make the powder mixture into pellets under 10 tons of load to ensure the pellet will not splash out during the arc-melting process. Melting the pellets has been carried out using a specially-designed and locally-made arc-melting furnace (Fig.1b) to produce button-shaped alloy samples. To ensure the chemical homogeneity, each button of the alloy samples has been arc melted for at least 5 (five) times. The buttons were 20 mm in diameter, 5 mm in thickness and about 3.5 – 6 grams in weight. The buttons were then ground to a mirror-like surface with SiC papers up to No. 2000 followed by 0.1 and 0.05 μm alumina powder. Finally, the ground surface of buttons was etched in a modified Kroll's reagent of 10 vol.% HF, 4 vol.% HNO_3 and 86 vol.% H_2O. Each of the alloys has been characterized using a LEO SUPRA 50VP SEM/EDS. Oxidation processes have been carried out on the samples in open air under isothermal condition of 900°C for 50 hours inside a muffle furnace. The weight gain of the samples during the oxidation process was determined, and cross-sectional microstructures of the samples have been characterized using SEM/EDS.

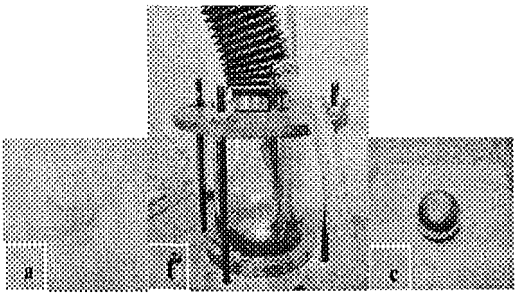

Fig.1. a) a cell of locally-made arc-melting furnace; b) a pellet of metals powder; and c) a button of alloy [13].

Table 1. Some selected compositional variations of alloys in at. %

Nominal alloy	*Compositional Variations*	*Ti (at. %)*	*Al (at. %)*	*Cr (at. %)*
1	Ti – 50Al	50	50	-
2	Ti – 53Al	47	53	-
3	Ti – 60Al	40	60	-
4	Ti – 65Al	35	65	-
5	Ti – 52Al – 5Cr	43	52	5
6	Ti – 45Al – 10C	45	45	10
7	Ti – 45Al – 15Cr	40	45	15
8	Ti – 42Al – 27Cr	31	42	27

RESULTS AND DISCUSSION

Selection of the Compositional Variations of Alloys

Compositional variations of the alloys were determined primarily based on the consideration of protective oxide scale formation on the surface of the alloys during oxidation processes. Brady M.P. et al. have indicated that binary titanium aluminides alloys require approximately 49 at.% Al to form a protective alumina scale at 800 – 1000°C in dry oxygen and 60 – 70 at.% Al in dry air [4,5]. Therefore the compositional variations of the binary alloys selected for this investigation have included Ti-50Al, Ti-53Al, Ti-60Al and Ti-65Al and grouped them together as series 1.

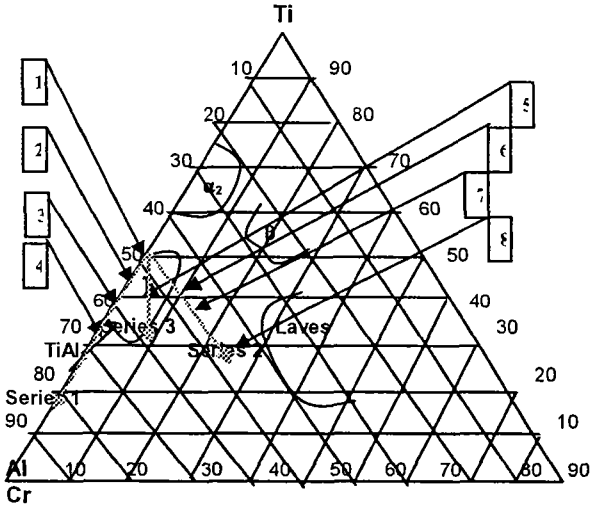

Fig.4. Ternary phase diagram of Ti-Al-Cr with initial compositional variations of alloys mapped (1:Ti-50Al; 2:Ti-53Al; 3:Ti-60Al; 4:Ti-65Al; 5:Ti-52Al-5Cr; 6:Ti-45Al-10Cr; 7:Ti-45Al-15Cr; 8:Ti-42Al-27Cr).

Previous investigations have indicated that Cr at a concentration of 8 – 10 at. % has a beneficial effect on the oxidation resistance of titanium aluminides alloys, however, addition of Cr at low concentrations (< 4 at. %) appeared to be detrimental during air exposure at temperature as high as 1000°C. The Cr effect was shown to be related to the formation of the Laves phase, $Ti(Cr,Al)_2$. Laves-based Ti-Al-Cr alloys have the supporting ability to form a protective alumina scale at 800 – 1300°C exposed in air despite an Al content of only 33 – 50 at.% [4, 5,12]. Series 2 which includes Ti-45Al-10Cr, Ti-45Al-15Cr, and Ti-42Al-27Cr alloy is selected to verify the results of earlier investigations.

Lastly, series 3, which consists of only Ti-52Al-5Cr alloy, will represent the intermediate alloy composition between series 1 and series 2. Details of the compositional variations of alloys for each series can be seen in Fig.4.

Alloys Phase Compositions and Microstructures

The chemical composition and microstructure of phases strongly affect some properties of the alloys including the oxidation resistance [10]. The two phase γ (TiAl) + α_2 (Ti_3Al) classes of titanium aluminides beside offers good mechanical properties, also demonstrates superior oxidation resistance [5]. Oxidation resistance in the alloys is related to the extent to which they are capable to form continuous and protective alumina (Al_2O_3) scales [4,5,6].

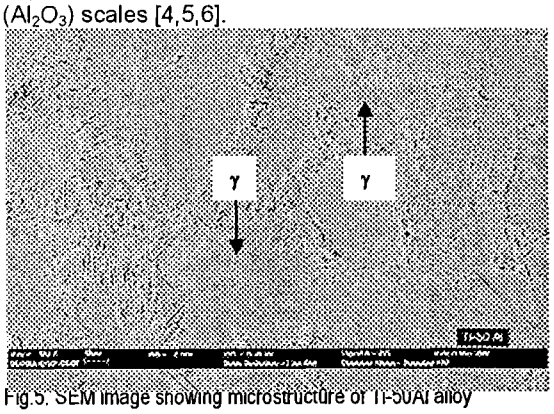

Fig.5. SEM image showing microstructure of Ti-50Al alloy

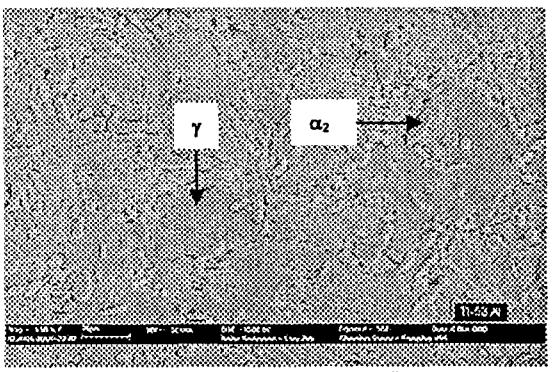

Fig.6. SEM image showing microstructure of Ti-53Al alloy

In this study the compositional variations of alloys is divided into 3 groups: series 1, 2, and 3. Series 1 is binary titanium aluminides alloys that consists of Ti-50Al, Ti-53Al, Ti-60Al, and Ti-65Al alloy. The binary titanium aluminides alloys represent the two-phase regions on either side of γ-TiAl phase (γ + α_2 and γ + $TiAl_2$). The microstructures of Ti-50Al and Ti-53Al alloys are fully lamellar and nearly lamellar, respectively. Ti-50Al alloy shows grains size of ~ 40 – 70μm coarser than ~ 20 – 30 μm in Ti-53Al alloy (see Fig.5 and Fig.6). The grains in Ti-50Al are of γ phase while in Ti-53Al alloy are of (γ + α_2) phase.

Accordingly, Ti-60Al as well as Ti-65Al alloy show the γ phase as the matrix and $TiAl_2$ being the precipitates (Fig.7 and Fig.8). However, the number of $TiAl_2$ grains in Ti-65Al alloy is much more than in Ti-60Al alloy. This is in agreement with the binary phase diagram of Ti-Al whereas $TiAl_2$ phase developed in region of Ti-65Al. Much more Al in Ti-60Al and Ti-65Al alloy has been used to form many alumina scales.

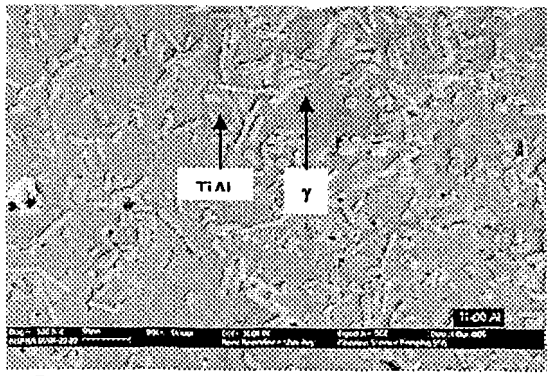

Fig.7. SEM image showing microstructure of Ti-60Al alloy

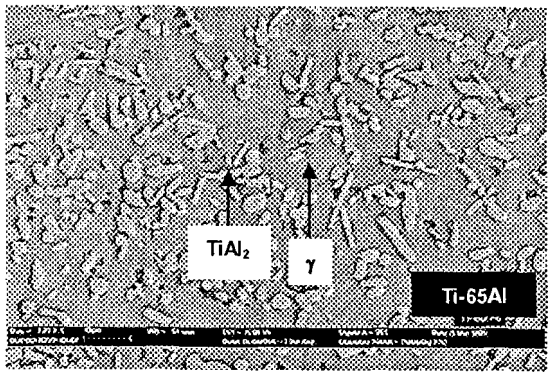

Fig.8. SEM image showing microstructure of Ti-65Al alloy

Series 2 includes Ti-45Al-10Cr, Ti-45Al-15Cr and Ti-42Al-27Cr alloy. The ternary Ti-Al-Cr alloys were selected based on the alumina-formation boundary according to Perkins and Meier, which is superimposed on the schematic Ti-Al-Cr phase diagram [6,9]. The microstructure of Ti-45Al-10Cr alloy, as well as Ti-45Al-15Cr alloy show β as the matrix and α_2 as precipitates while Ti-42Al-27Cr alloy shows Laves phase as the matrix and Ti as precipitates (see Fig.9, Fig.10, and Fig.11). The formation of Laves phase is needed to develop the protective alumina scale while β phase is needed to increase Al diffusivity in the alloys. It means that the activity of titanium to form TiO_2 oxide scale on the surface of the alloys is reduced. Both can be obtained through alloying addition of chromium and for that purpose chromium is chosen as alloying addition.

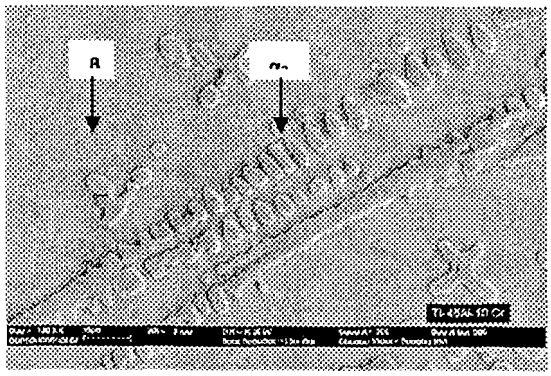

Fig. 9. SEM image showing microstructure of Ti-45Al-10Cr alloy

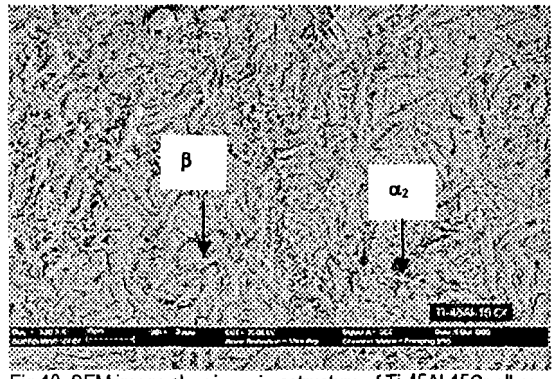

Fig.10. SEM image showing microstructure of Ti-45Al-15Cr alloy

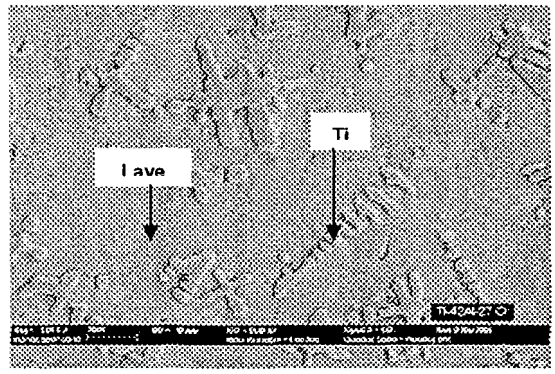

Fig.11. SEM image showing microstructure of Ti-42Al-27Cr alloy

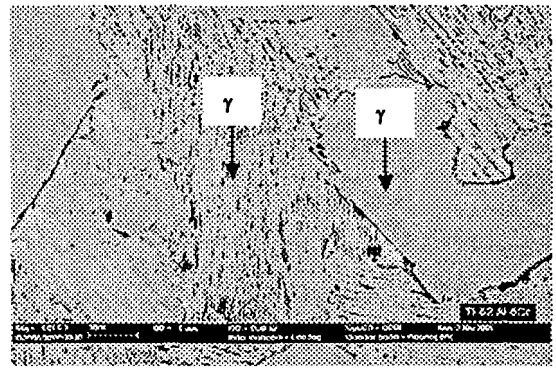

Fig.12. SEM image showing microstructure of Ti-52Al-5Cr alloy

Ti-52Al-5Cr alloy in series 3 is composed of series 1 and series 2. The microstructure of this alloy is similar to Ti-50Al alloy which is fully lamellar. The grains size of Ti-50Al alloy is the same with Ti-52Al-5Cr alloy which is ~ 40 – 70 μm. It consists of $\gamma + \alpha_2$ grains (Fig.12).

Result of EDS Test

Using Energy Dispersive Spectroscopy (EDS), quantitative assessment of the phases present in each of the alloys can be obtained (Table 2). EDS test was carried out with SUPRA 50VP-23-57. Based on the compositional result, each of the existing phases can readily be identified.

Table 2. Phase compositions sample analysis by using Energy dispersive X-ray) System (EDS).

Name of Samples	*Phase*	*At. % Titanium*	*At.% Aluminum*	*At.% Chromium*
Ti-50Al	γ (TiAl)	45.70 – 53.99	46.01 – 54.30	-
Ti-53Al	γ (TiAl)	51.41	48.59	-
	α_2 (Ti_3Al)	66.62	33.38	-
Ti-60Al	$TiAl_2$	41.01	58.99	-
	γ (TiAl)	53.06	46.94	-
Ti-65Al	$TiAl_2$	41.94	58.06	-
	γ (TiAl)	51.04	48.96	-
Ti-52Al-5Cr	γ (TiAl)	41.42 – 42.50	49.84 – 55.05	3.01 – 7.65
Ti-45Al-10Cr	β (B2)	52.08	36.06	11.86
	α_2 (Ti_3Al)	87.29	11.27	1.44
Ti-45Al-15Cr	α_2 (Ti_3Al)	73.74	23.84	2.42
	β (B2)	42.14	48.85	9.01
Ti-42Al-27Cr	Laves	33.29	36.92	29.79
	Ti	100.00	-	-

Results of Oxidation Test

Alloys selected to be subjected to the oxidation process in air at 900°C for 50 hours are Ti-50Al, Ti-60Al, Ti-45Al-10Cr, Ti-52Al-5Cr and Ti-42Al-27Cr alloys.

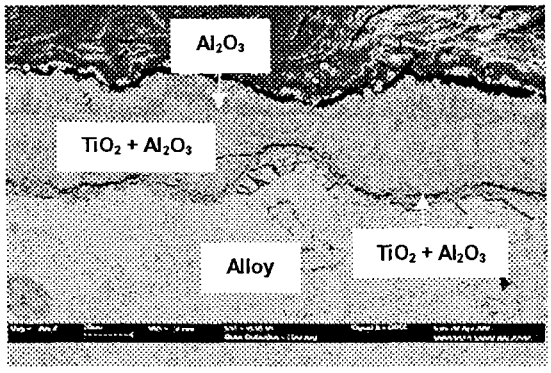

Fig.13. Cross-sectional microstructures of Ti-50Al alloy after oxidation in air at 1173K for 50 hours

Fig.13. presents the oxidation results on Ti-50Al alloy. The microstructures of the alloy are still fully lamellar as the initial alloy. While the grains have become finer after the oxidation process, its chemical composition remained unaltered. Two types of oxide scales have been produced as the results of the oxidation process, (TiO_2 + Al_2O_3) and Al_2O_3. The thickness of the (TiO_2 + Al_2O_3) mixed scale is ~ 37.5 μm while the alumina scale in this mixed scale is ~ 5 μm thick. The existence of a protective alumina scale in the Ti-50Al alloy is contrary to the previous investigation which claimed that approximately 60 – 70% at.% Al is needed for binary Ti-Al alloys to form a protective alumina scale in air [4,5].

For Ti-60Al alloy, however, the surface layer of the oxide scale is made of ~ 5 μm thick TiO_2 scale sitting on top of the alumina layer with thickness of ~ 3 – 4 μm (Fig.14). The (TiO_2 + Al_2O_3) scale of ~ 25 μm thick is also present beneath the previously mentioned outer scale.

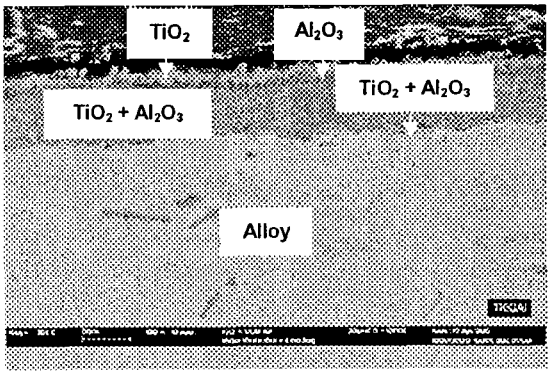

Fig.14. Cross-sectional microstructures of Ti-60Al alloy after oxidation in air at 1173K for 50 hours

Similar situation occurred for Ti-52Al-5Cr alloy having layers of TiO_2 scale on the surface, followed by Al_2O_3 scale between the surface layer and the inner layer of mixed (TiO_2 + Al_2O_3 + Cr_2O_3) scale (Fig.15). The thickness of the scales is ~ 12.5 μm, ~ 5 μm and ~ 50 μm for TiO_2, Al_2O_3 and mixed scale, respectively. The fully lamellar microstructure of the bulk alloy, before and after oxidation remained unchanged. The black nodules in the bulk alloy are identified as alumina.

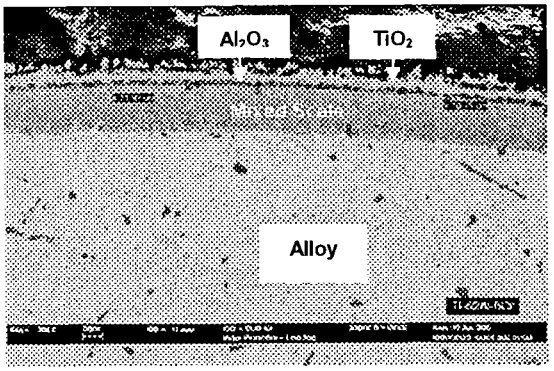

Fig.15. Cross-sectional microstructures of Ti-52Al-5Cr alloy after oxidation in air at 1173K for 50 hours

The cross-sectional microstructure of Ti-45Al-10Cr alloy is given in Fig.16 showing only one mixed scale exists on the surface of the alloy with a thickness of ~ 60.37 μm. Within the bulk alloy particles of TiN/TiC can be identified. The formation of TiN particles, which interrupts the establishment of a continuous alumina scale, is considered to be detrimental due to the inability of the alloy to form a protective alumina scale.

Fig.17. shows the cross-sectional microstructures of Ti-42Al-27Cr alloy. It can be seen that alumina scale interrupts the (TiO_2 + Al_2O_3) scale with a thickness of ~ 3 μm while a thickness of (TiO_2 + Al_2O_3) scale is ~ 9.82 μm. The existing mixed scale in this alloy is still not dense. The dark spot in the mixed scale is identified as the TiO_2-rich mixed (TiO_2 + Al_2O_3 + Cr_2O_3) scale, while the light spot is the Cr_2O_3-rich mixed scale.

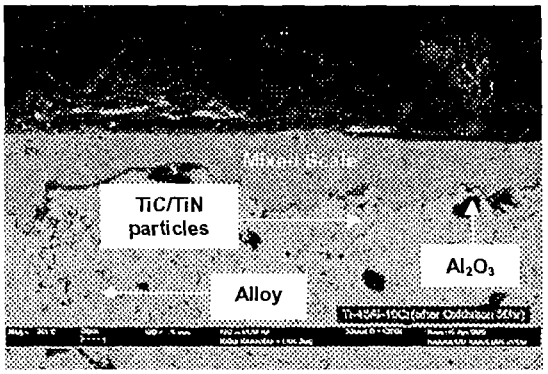

Fig.16. Cross-sectional microstructures of Ti-45Al-10Cr alloy after oxidation in air at 1173K for 50 hours

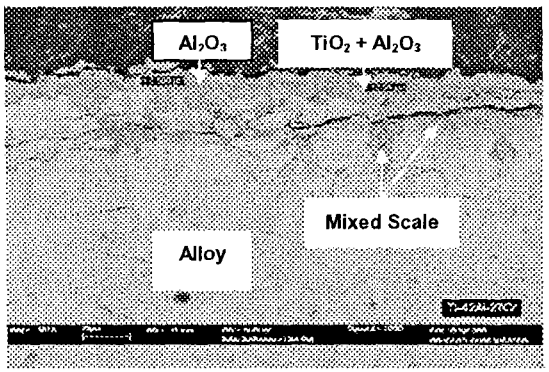

Fig.17. Cross-sectional microstructures of Ti-42Al-27Cr alloy after oxidation in air at 1173K for 50 hours

From the observed weight-gain experienced by the alloys, Ti-42Al-27Cr alloy has the lowest oxidation rate with only 0.20% increased weight for the formation of its oxide scales whereas the highest oxidation rate belongs to Ti-45Al-10Cr alloy with a 1.43% weight increase. In the intermediate range, Ti-50Al, Ti-60Al and Ti-52-Al-5Cr alloys exhibit increased weight of 0.85%, 0.67% and 0.70%, respectively. The highest oxidation rate experienced by Ti-45Al-10Cr alloy is due to its inability to form a protective alumina scale on its surface. It is postulated that ternary additions of 10 at.% Cr to form the β phase is not sufficient to reduce the oxygen permeability in the alloy. However, it has been observed that protective alumina scale was formed in Ti-42Al-27Cr, Ti-50Al, Ti-60Al and Ti-52Al-5Cr alloy. Unfortunately, each of the alloys suffers internal attack with increased penetration of oxygen beneath the scales.

CONCLUSIONS

Alloys phase composition and microstructures can affect the properties of alloys including its oxidation resistance. Alloying addition of 27 at.% Cr to 40 – 45 at.% Al with the presence of Laves phase is observed to improve the oxidation resistance of titanium aluminides alloys. However, 10 at.% Cr is detrimental with the formation of β phase.

Acknowledgement

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